



# **PIMS**

## **Apatite II Treatment of Metal-Contaminated Water along the U.S.-Mexican Border**

**(Pb, Zn, Cd, Cu, Al, SO<sub>4</sub>,  
NO<sub>3</sub> and others)**

**Dr. James L. Conca, New Mexico State University at the  
Carlsbad Environmental Monitoring and Research Center**

**and**

**Dr. Judith Wright, PIMS NW, Inc., Carlsbad, New Mexico**

- **The Center for Excellence in Hazardous Materials Management (CEHMM) provides seed funding in Carlsbad, New Mexico, to develop business in hazardous materials treatment, handling and disposal, especially along the border region between the United States and Mexico.**
- **The Carlsbad Environmental Monitoring and Research Center, in the College of Engineering at NMSU is a research center devoted to the detection, monitoring, and behavior of hazardous and radiological constituents in the environment**
- **PIMS NW, Inc. is a small women-owned business based in Carlsbad, New Mexico, that has developed innovative technologies for the remediation of hazardous constituents, particularly heavy metals such as Pb, Zn, Cd, Cu, and other species such as SO<sub>4</sub>, NO<sub>3</sub> and perchlorate. Apatite II is a reactive material specifically developed to remediate metals.**

## Project Goal

- ❖ **Demonstrate this technology at a site chosen in cooperation with BECC and TCEQ.**
- ❖ **Based on the results, determine the number of sites along the border that can utilize this technology, depending upon its cost and effectiveness, e.g.,**
  - **\$40/million gallons of water with Pb at 1 mg/L (ppm)**
  - **\$22/ton of contaminated soil with Pb > 1000 mg/kg (ppm)**
  - **holds over 20% of its weight in metals, permanently**

## **PIMS: Phosphate-Induced Metal Stabilization Technology Description**

**Take a reactive form of the phosphate mineral group, apatite, and place it in contact with metal-contaminated water, e.g., groundwater, waste streams, soil leachates. Most metals in solution will be immobilized on the apatite mineral by precipitation (U, Pb, Pu, lanthanides), co-precipitation (transition metals) or by surface sorption (most metals).**

**The apatite can be containerized or free-standing in a trench or culvert as a permeable reactive barrier (PRB).**

# The Apatite Mineral Group



F, Cl, Br, CO<sub>3</sub>, X

CO<sub>3</sub>, SO<sub>4</sub>, SiO<sub>4</sub>, XO<sub>y</sub>

Pb, U, Zn, Cd, Th, Cr, Co, Na, Ni,  
Sr, Rb, Zr, Cs, REE, Au, Ba, Ir, Hg,  
Se, As, Ta, Fe, and others

# Apatites compared to soluble phosphates

## ✦ Other phosphate phases are too soluble

- Are not persistent in the subsurface, e.g., phosphate fertilizers and phosphoric acid
- Require large excesses of  $\text{PO}_4^{3-}$  and metal concentrations in solution and may produce microbial blooms

## ✦ Process requires nucleation sites

- Surfaces of the apatite mineral structure provide nucleating sites for precipitation of metal-apatite mineral species thus overcoming large activation energies

## ✦ Apatites are stable in the subsurface

- Over geological time - millions of years
- Persist in the face of subsurface processes and diagenesis
- Do not induce microbial blooms

## ✦ Apatites are also good non-specific surface sorbers

## Apatite-Pyromorphite-Phosphate Mineral Solubility Constants

$\text{Pb}_5(\text{PO}_4)_3(\text{OH}, \text{Cl}, \text{F})$	$\log K_{\text{sp}} \ll -76.5$
$\text{Ca}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 10\text{H}_2\text{O}$	$\log K_{\text{sp}} \sim -49.0$
$\text{UO}_2\text{HPO}_4$	$\log K_{\text{sp}} \sim -10.7$
$\text{Zn}_3(\text{PO}_4)_2$	$\log K_{\text{sp}} \sim -35.3$
$\text{Cd}_3(\text{PO}_4)_2$	$\log K_{\text{sp}} \sim -32.6$
$\text{Am}(\text{PO}_4)$	$\log K_{\text{sp}} \sim -24.8$
$\text{Pu}(\text{PO}_4)$	$\log K_{\text{sp}} \sim -24.4$
$\text{Sr}_5(\text{PO}_4)_3(\text{OH})$	$\log K_{\text{sp}} \sim -51.3$

## Other Common Mineral Solubility Constants

Salt (NaCl)	$\log K_{\text{sp}} \sim 0.0$
Quartz ( $\text{SiO}_2$ )	$\log K_{\text{sp}} \sim -4.0$

## **The search for the best apatite to remediate metals included:**

- ◆ **North Carolina phosphorite rock**
- ◆ **Florida phosphorite rock**
- ◆ **Permian Phosphoria Formation phosphorite rock**
- ◆ **Durango apatite (igneous)**
- ◆ **Cow bone**
- ◆ **Bone char**
- ◆ **Cannery waste**
- ◆ **Reagent grade tricalcium phosphate**
- ◆ **Synthetic apatites**
- ◆ **Apatite II**

## What is Apatite II?

Made from  
processed fish bones,  
the nominal  
composition of  
Apatite II is:



where  $x < 1$ .



# Apatite II compared to other apatites

## ✦ Most apatites are less effective

- recrystallized - less reactive
- fully fluorinated - less reactive
- little microporosity - less reactive
- no carbonate - less reactive
- high existing metal content

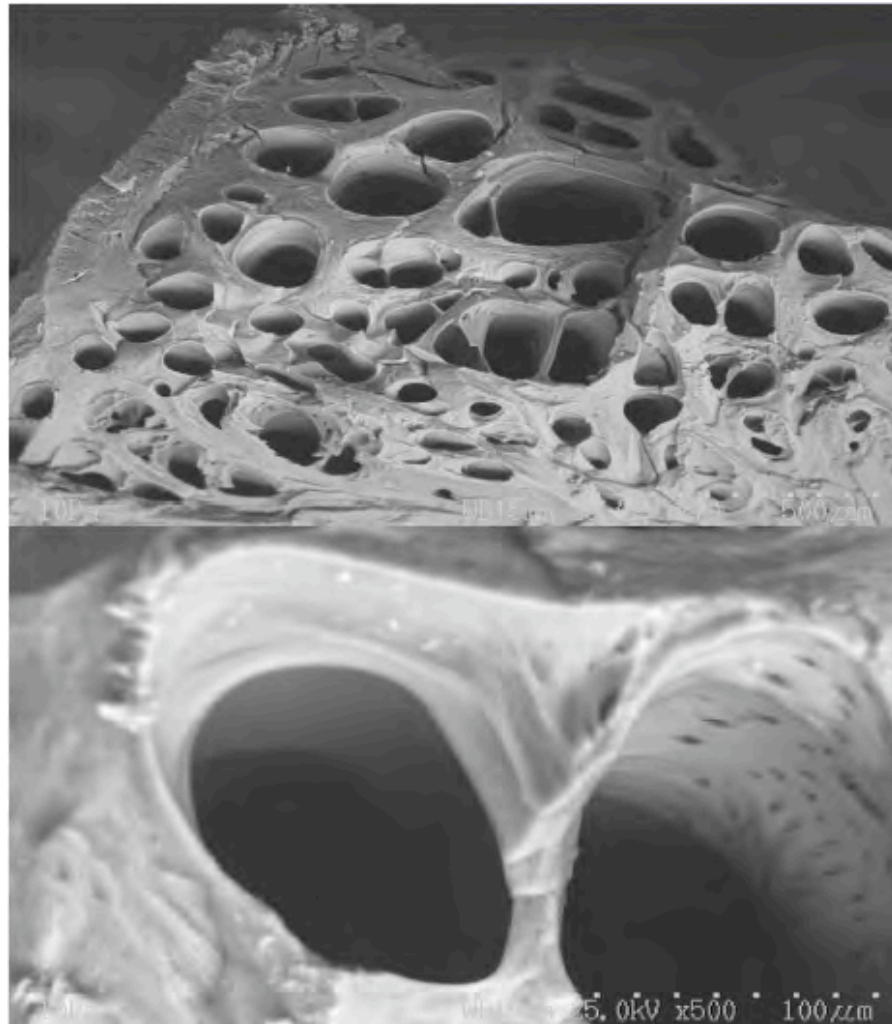
## ✦ Apatite II is the best

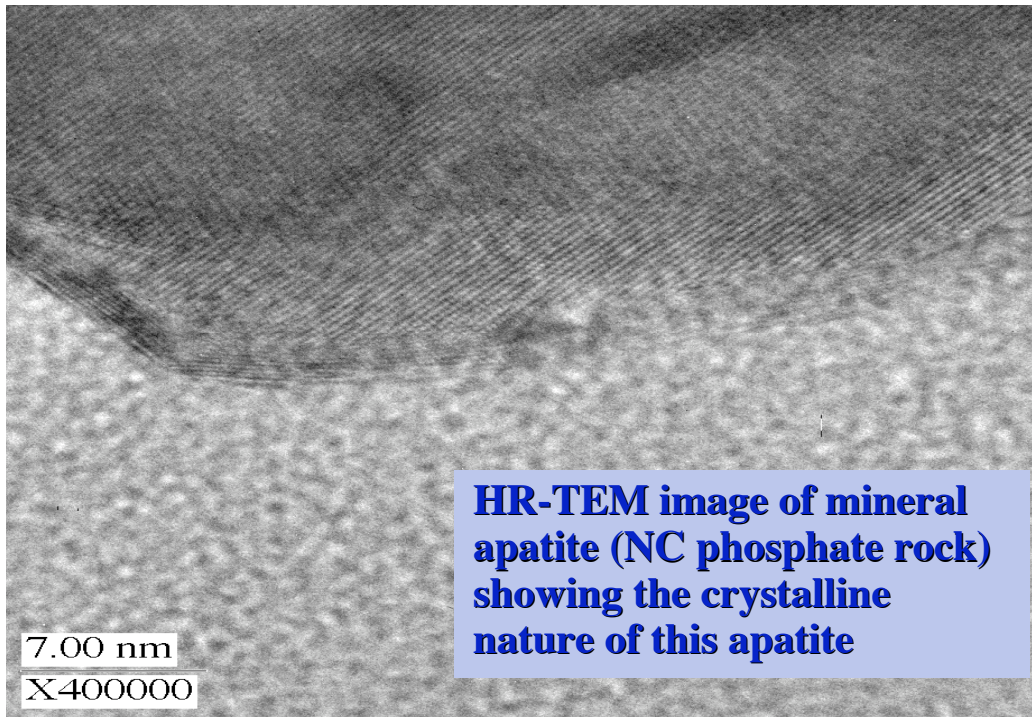
- fully carbonated - most reactive
- no fluorine and low trace metal content
- microporous - most reactive
- amorphous with random nanocrystals
- inexpensive and abundant

## ✦ Apatite II can sequester over 20% of its weight in metals, particularly Pb, U and Pu

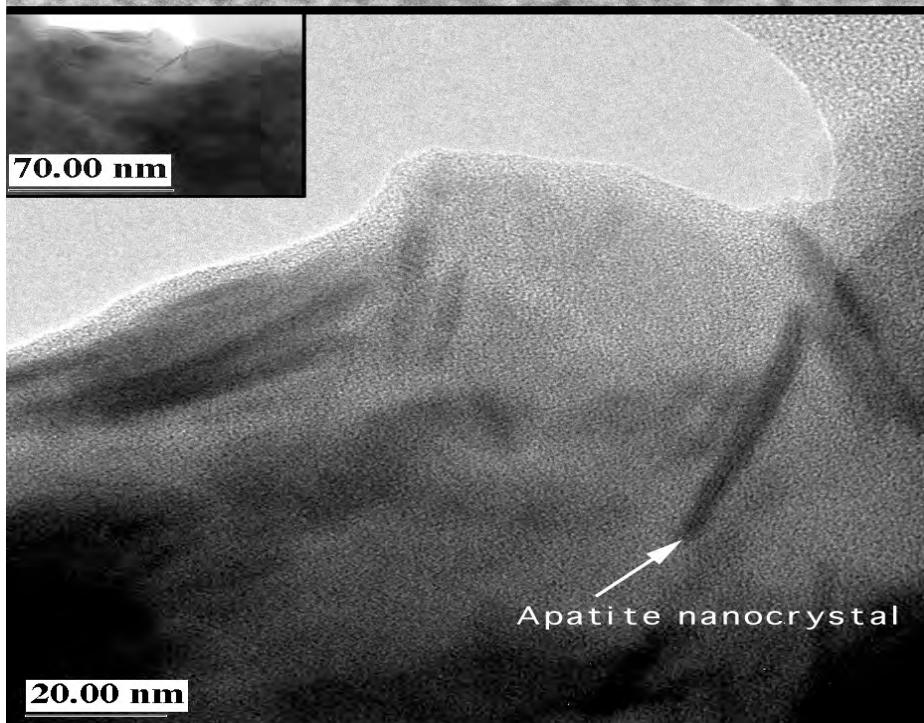
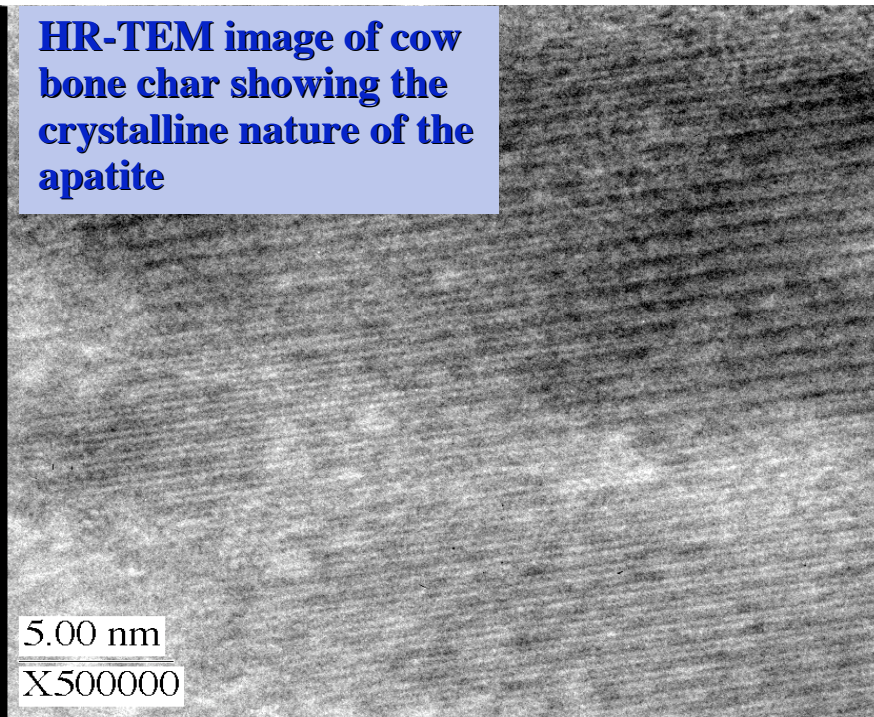
## Apatite II works by four general non-mutually-exclusive processes, depending upon the metal, the concentration of the metal and the aqueous chemistry of the system

- ◆ **Heterogeneous nucleation--** supplying a small amount of  $\text{PO}_4$  to solution to exceed the solubility limits of most metal apatites
- ◆ **At low pH, acts as a buffer--** neutralizes acidity to pH 6.5-7 causing precipitation of many metal apatites
- ◆ **Chemi-adsorption--** uncompensated  $\text{PO}_4$  and  $\text{OH}^-$  groups on the surface induce metal sorption, particularly transition metals
- ◆ **Biological stimulation--** P and bioavailable organics can stimulate microbial community activity in many chemical systems, e.g, high  $\text{SO}_4$  or  $\text{NO}_3$





HR-TEM image of cow bone char showing the crystalline nature of the apatite



HR-TEM image of Apatite II showing general amorphous nature with random nanocrystal inclusions of crystalline apatite

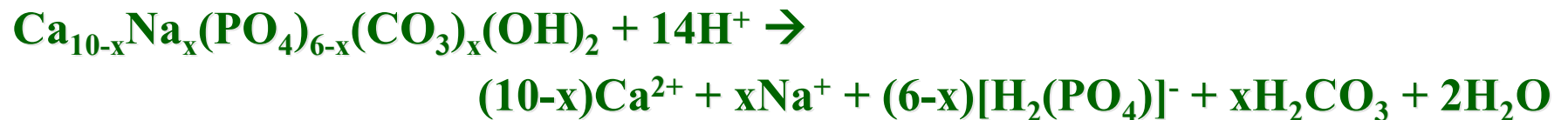
## How PIMS using Apatite II stabilizes Pb

The process consists of two steps:

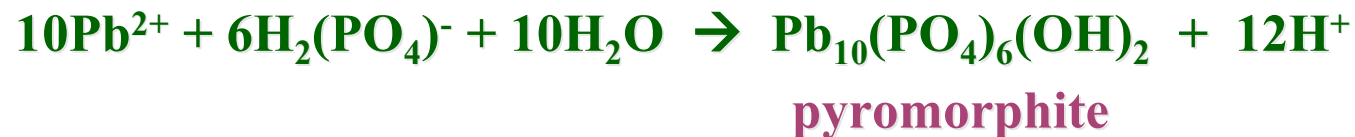
### 1) a dissolution reaction

Apatite II provides phosphate to solution...

Apatite II



### 2) a precipitation reaction on the Apatite II seed crystal ...causing pyromorphite, to precipitate on Apatite II surfaces.



Similar reactions occur for U and Pu

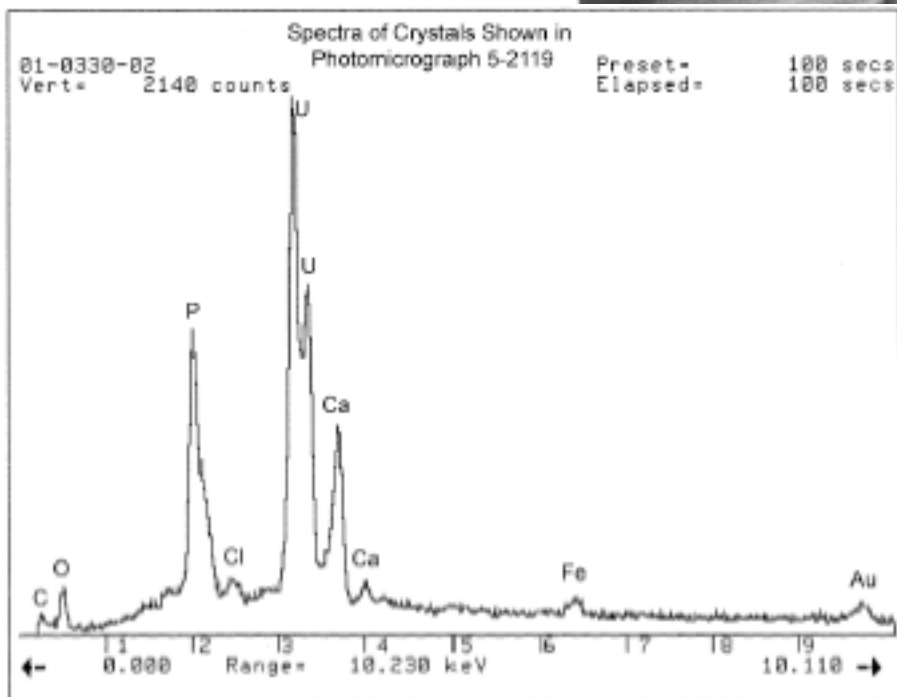


**SEM image of pyromorphite crystals precipitated on  
primary apatite (Lower, 1998)**

## Precipitation of Pb-pyromorphite from solution

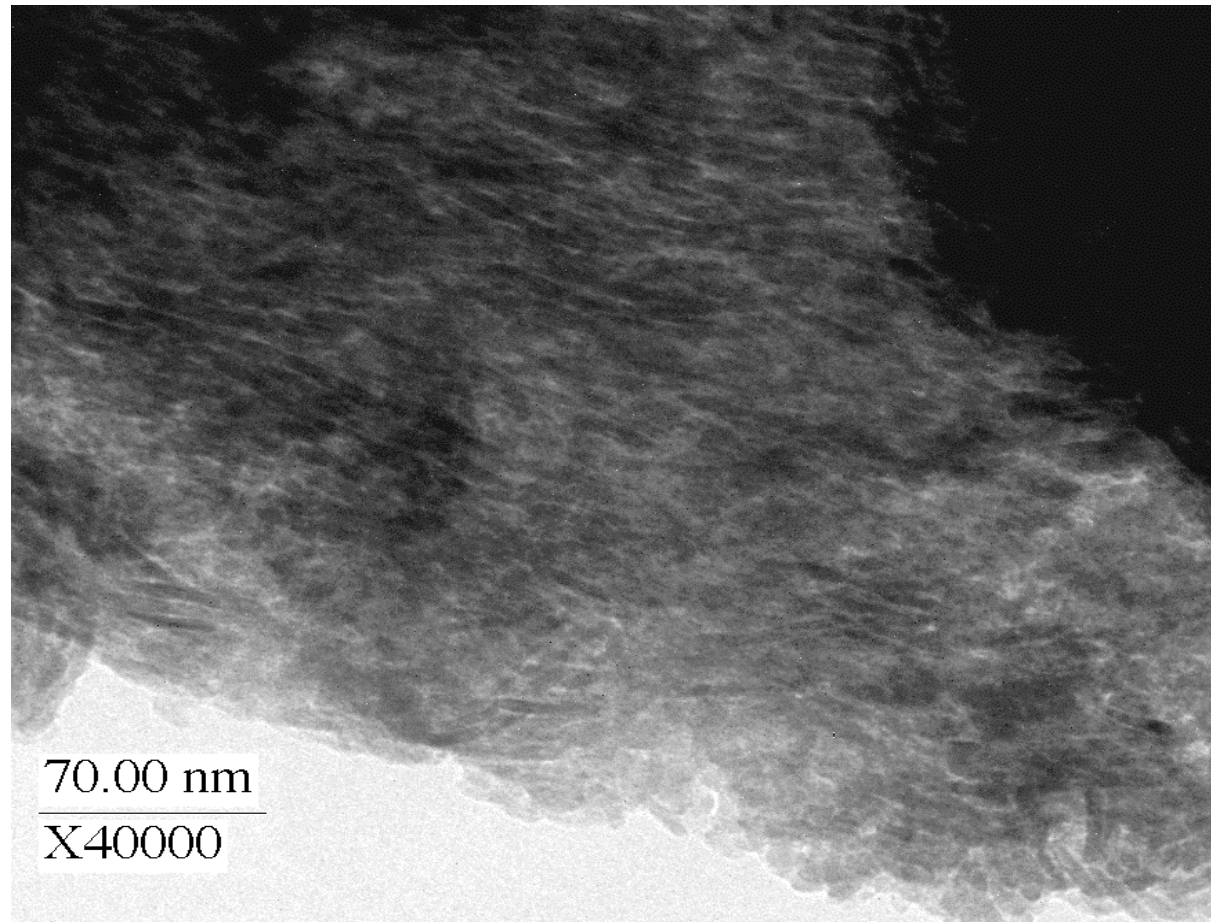
- **homogeneous nucleation** (direct ppt without seed crystals)  
occurs only at high Pb concentrations,  $> 10$  mg/L Pb
- **heterogeneous nucleation** (ppt onto seed crystals)  
occurs at low Pb concentrations,  $< 10$  mg/L Pb  
and dominates under environmental conditions
- Precipitation of a pyromorphite in the environment almost always requires a seed crystal of an apatite mineral
- Soluble phosphates, e.g., fertilizers or phosphoric acid, do not work well under most environmental conditions
- Pb sorbed or complexed with non-apatite phosphates can later remobilize

**SEM-EDS  
photomicrograph of  
a uranium-rich  
precipitate on  
Apatite II from Oak  
Ridge Y-12 site.**



**The plate-like structure and spectra  
indicate autunite.**

**HR-TEM image of Apatite II after treatment of leachate from uranium-contaminated soil during the soil washing operation at LANL. Uranium is completely covering the surface of the Apatite II**



- ◆ **Precipitation of a stable solid phase in the environment requires a seed crystal of apatite or autunite mineral.**
- ◆ **Soluble phosphates (fertilizers) or precursors (phosphoric acid) will not work under environmental conditions.**
- ◆ **Sorbed or complexed metals will later remobilize, as has been observed for Pb at military firing ranges.**

**For systems having sulfate, nitrate, perchlorate or other electron acceptors, biological stimulation by Apatite II can dominate:**

- 1) Apatite II provides an optimal amount of phosphate, carbon and other essential nutrients continuously to solution for microbial sulfate reduction**



- 2) Sphalerite (and other metal sulfides) precipitate on Apatite II surfaces rapidly**



**The CH<sub>2</sub>O represents the organic carbon from the Apatite II that serves as both electron donor and carbon source for the sulfate reducers**

**Untreated soil from an industrial site with >10,000 ppm Zn, consistently barren to all plant species attempted; lettuce, geranium, char, fescue, clover and lolium (shown here) while the Apatite-treated (5%) soil was prolific to all species.**



**Plant growth studies show that the addition of 5% Apatite II by weight to the soil reduces the toxic effects of many contaminants**

## **Nevada Stewart Mine Adit (Zn-contaminated outflow)**

**animal toxicity studies:** *Ceriodaphnia dubia*, a freshwater invertebrate  
*Pimephales promelas*, the fathead minnow

### **Untreated outflow:**

**No Observed Acute Effect Level (NOAEL)**

**= 1.6% for *C. dubia* (completely lethal)**

**= 12.5% for *P. promelas* (highly lethal)**

**Fifty-percent Lethal Concentration (LC<sub>50</sub>)**

**= 2.2% for *C. dubia***

**= 26.4% for *P. promelas***

### **after Apatite II Treatment Tank:**

**No Observed Acute Effect Level (NOAEL)**

**= 100% for *C. dubia* (completely non-lethal)**

**= 100% for *P. promelas* (completely non-lethal)**

**Fifty-percent Lethal Concentration (LC<sub>50</sub>)**

**= 95% for *C. dubia* (completely lethal)**

**= 100% for *P. promelas* (highly lethal)**

**no different than the control samples.**

## **Two Types of Field Application to water:**

**Treatment Tank - U, Cd, Zn, Cu, Tc, PCBs in Kentucky**

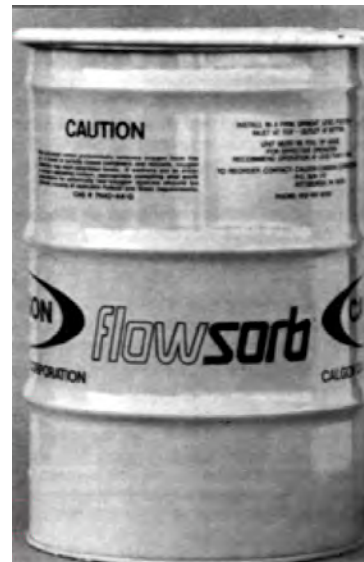
**Permeable Reactive Barriers - Pb, Cd, Zn in Idaho**

**This technology can also be directly applied to contaminated soils and waste by simple mixing.**

## GAC systems

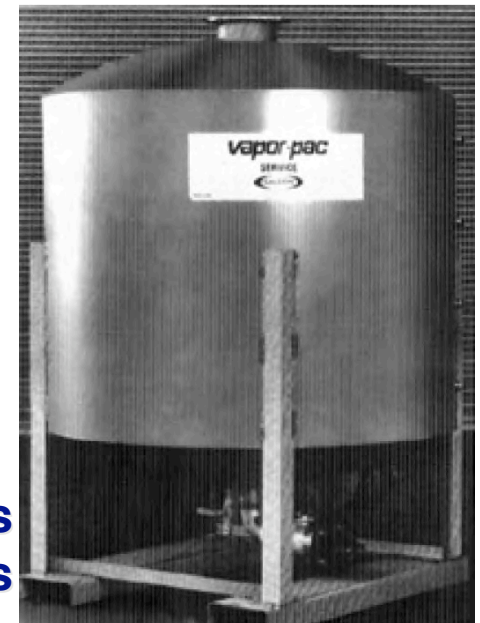
Treatment tanks can be any size to fit any application and flow rate

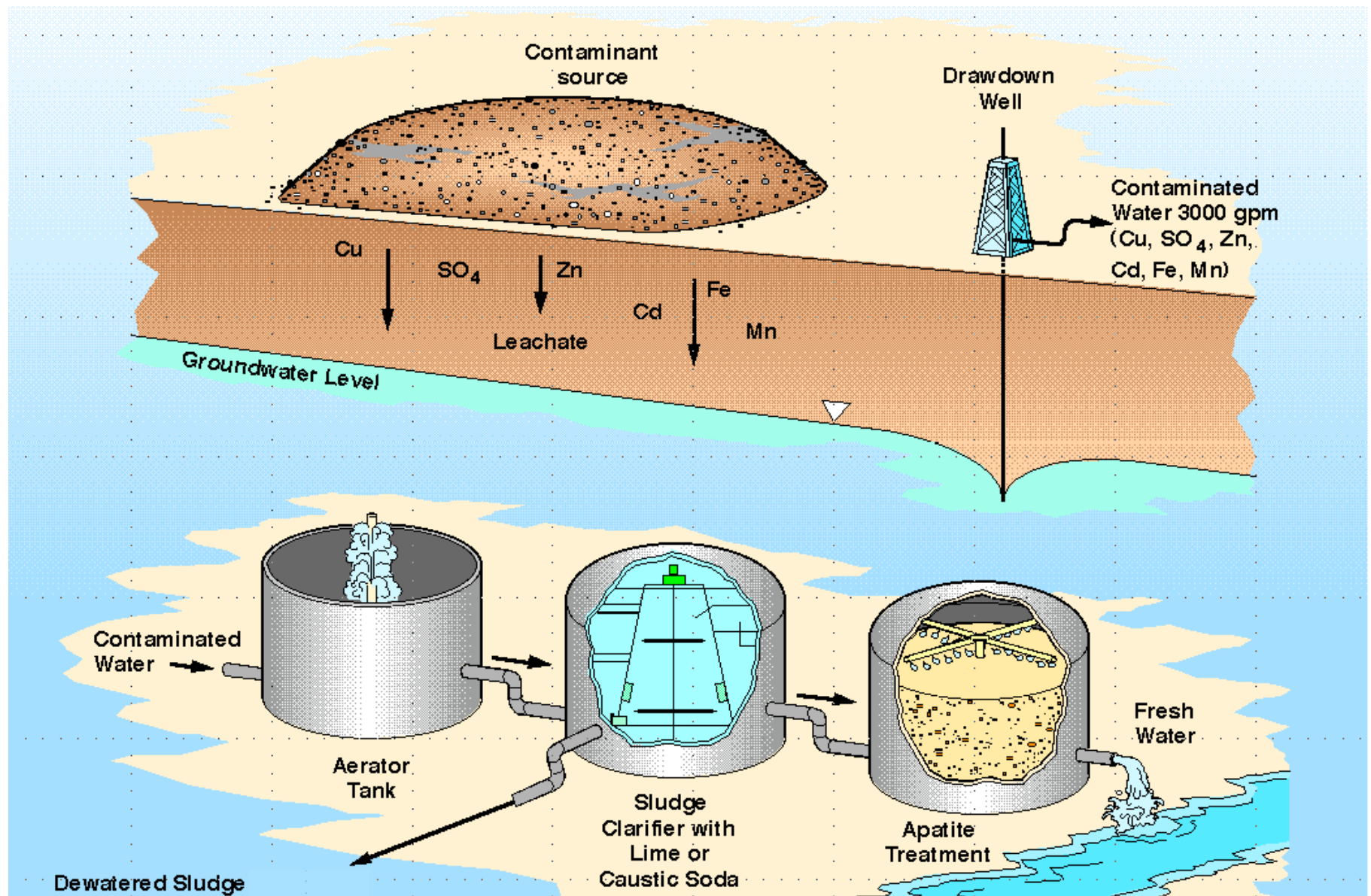
### 55-gallon drums



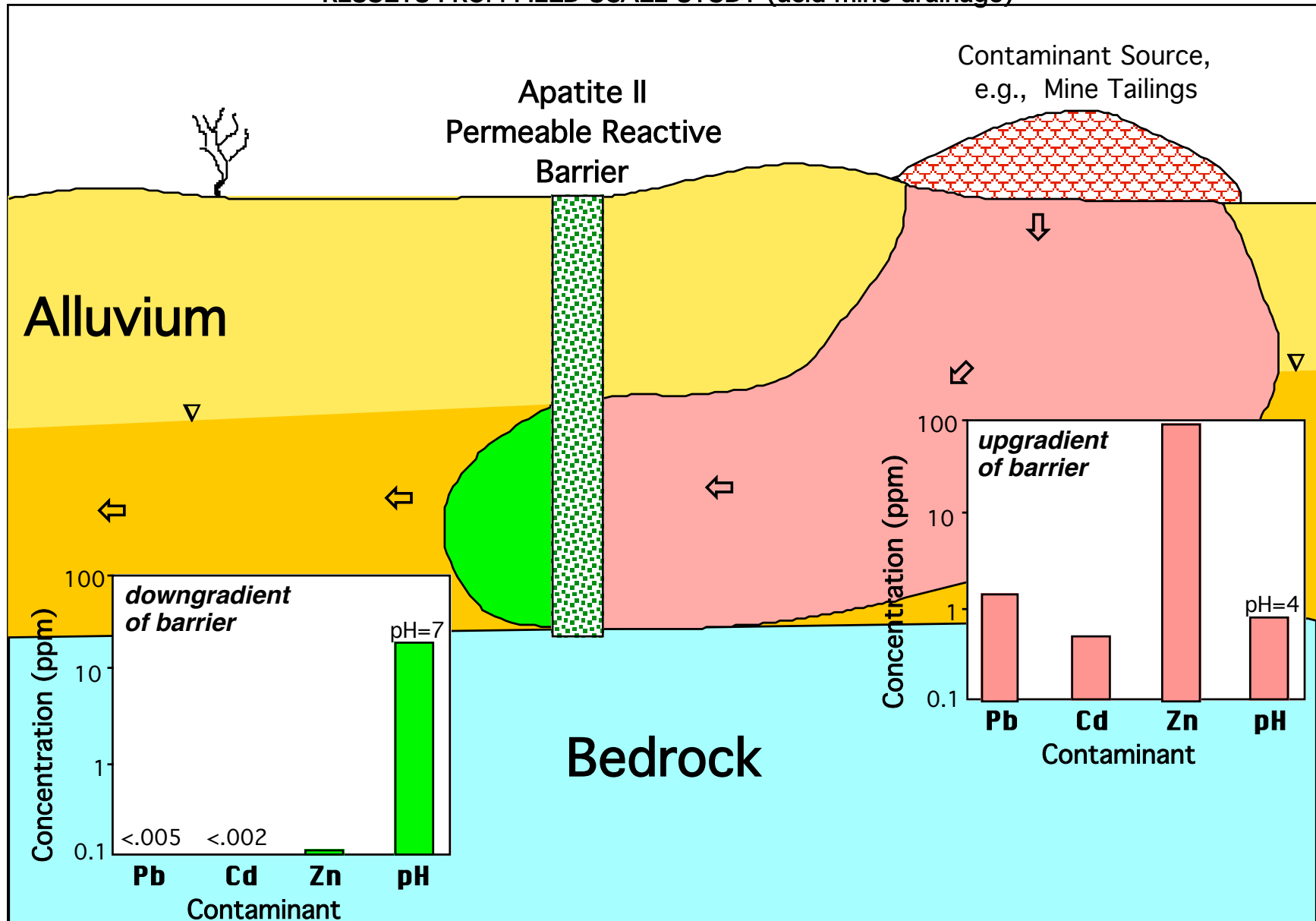
Apatite II can also be applied as an additional step in traditional wastewater treatment systems

larger treatment tanks  
>1000 gallons





# RESULTS FROM FIELD SCALE STUDY (acid mine drainage)



## **Tank Case History: Paducah Site**

- ◆ **In 2001, a fire sprinkler system froze and flooded the basements of two former process buildings.**
- ◆ **Flood water contained uranium (U), cadmium (Cd), zinc (Zn), copper (Cu), technetium (Tc), and detectable amounts of polychlorinated biphenyls (PCBs).**
- ◆ **Because of the elevated amounts of Cd present, the water was designated RCRA waste and, thus, could not be taken to the site's normal process water treatment system.**

## Feasibility Study

- ◆ An **Apatite II** mobile treatment system was designed to remove the COC to DOE-mandated discharge levels, e.g., 10% of applicable discharge limits mandated by the state.
- ◆ The pilot-scale treatment system consisted of columns with:
  - coal carbon for the PCBs and Tc
  - **Apatite II** for the U, Cd, Zn and Cu
  - controlled pumping and flow maintained flow rate and contact time
  - appropriate filtration systems
- ◆ Feasibility results indicated that the system would remove over 99% of the contaminants.

## The Mobile **Apatite II**/Carbon Reactive Treatment Tank at Paducah

- ◆ **Apatite II** system treated > 100,000 gallons of RCRA metal and radioisotope-contaminated wastewater
- ◆ All of the treated water has met DOE-mandated discharge limits.



- ◆ **Apatite II** system was more cost-effective and efficient than competing technologies, e.g., ion exchange, reverse osmosis, or ultra-filtration.
- ◆ Average removal efficiencies in the **Apatite II** were:
  - $\geq 99.7\%$  for U
  - $\geq 99.5\%$  for Cd
  - $\geq 99.7\%$  for Zn and Cu
- ◆ A secondary benefit of using **Apatite II** was significantly less secondary waste generation.

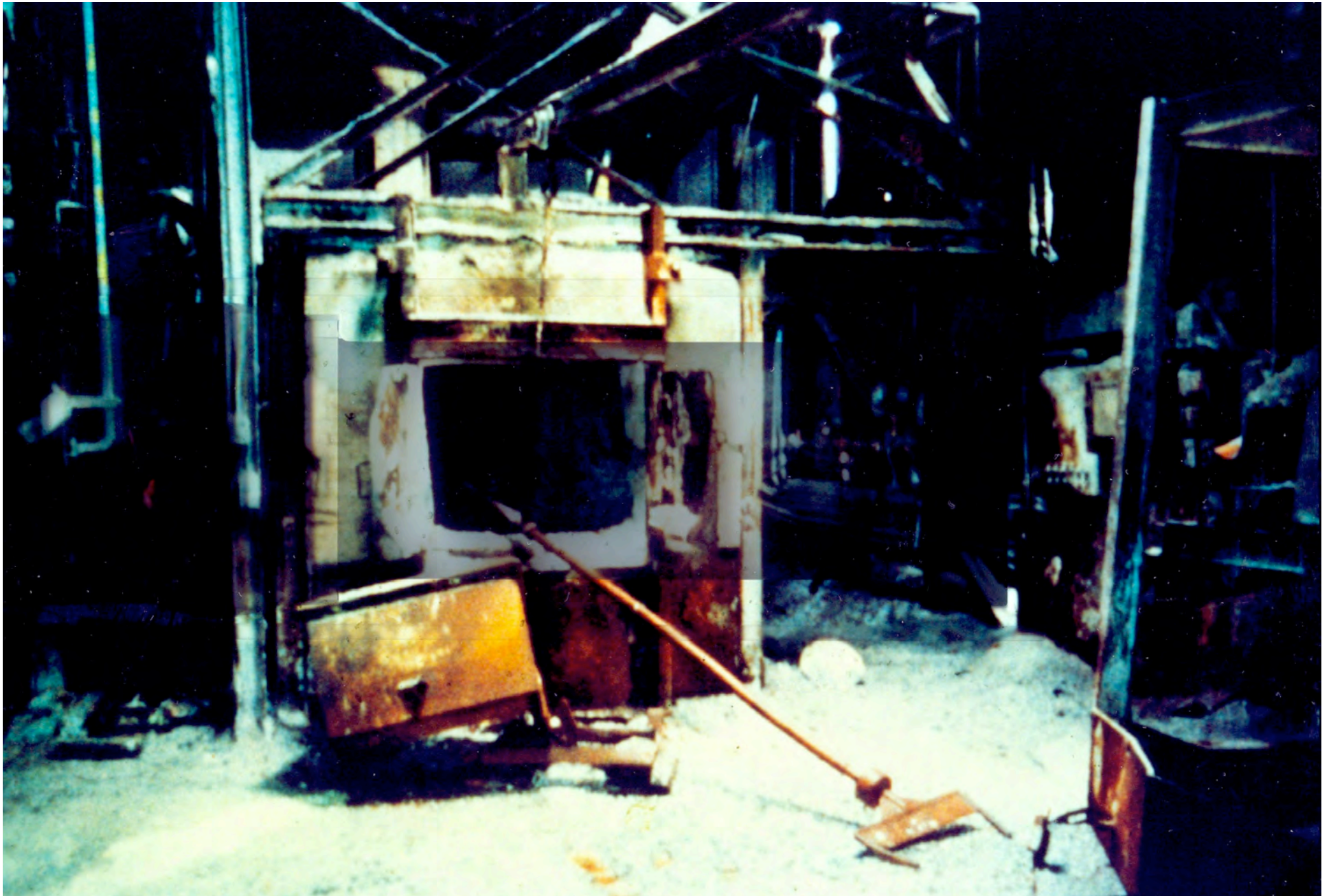


## **PRB Case History**

**Success Mine and  
Mill Site, Idaho**



**Environmental degradation through Pb particulate and vapor deposition  
in Smelterville, Idaho**



**Inside the smelter at Smelterville**

# **Success Mine and Mill Site**

**Operated from 1886 to 1956 in Northern Idaho**

**Over 500,000 ton tailings pile adjacent to the east fork of Ninemile Creek.**

**Soils: Pb, Zn, Cu and Cd at levels of 1000-4000 mg/kg**

**Groundwaters and surface seeps (mg/L or ppm)**

**250 ppm Zn**

**10 ppm Pb**

**1 ppm Cd**

**20 ppm Cu**

**Based on the feasibility studies of treating soils and groundwater, Idaho DEQ decided to put in a permeable reactive barrier of Apatite II between the Success Mine tailings and Nine Mile Creek**



**Success Mine tailings pile with Ninemile Creek in foreground.  
Apatite II PRB is off to the right between pile and creek**

## *Cd, Pb and Zn Levels in groundwater between the tailings and EFNC*

<i>Dissolved Analyte</i>	<i>Concentration Range (ppb)</i>	<i>Drinking Water* Criteria (ppb)</i>	<i>Aquatic Criteria†(ppb)</i>
cadmium	8 - 1,250	5	1
lead	70 – 1,440	15	2.5
zinc	4,850 – 177,000	5,000	100

*\*Federal Maximum Contaminant Level (MCL) for protection of drinking water.*

*†State chronic criteria for the protection of fresh water aquatic life.*

# PRB Construction

**445-meter long pressure grouted containment wall installed down to bedrock along edge of creek.**

**4.2-meter high, 4.6-meter wide, 15.4-meter long PRB vault made of Type V Portland cement was constructed to receive seep and alluvial groundwater flow. Vault is baffled to insure even, saturated flow. Discharge from vault occurs onto a rock apron before entering the creek. Plumbed and valved to allow sampling and replacement of reactive media.**

**Construction completed January 2001.**

**100 tons of Apatite II was used at a cost of \$350/ton**

**PRB is performing better than anticipated**



**Construction of PRB vault between East Fork of  
Ninemile Creek and the Tailings Pile.**



**Installation of the Apatite II in the baffles of the PRB vault.**



**Completed PRB vault at Success Mine. Flow is from bottom of photo to top and into Ninemile Creek behind.**

## Dissolved Metal Concentrations Entering and Exiting the Apatite II Permeable Reactive Barrier at Success Mine

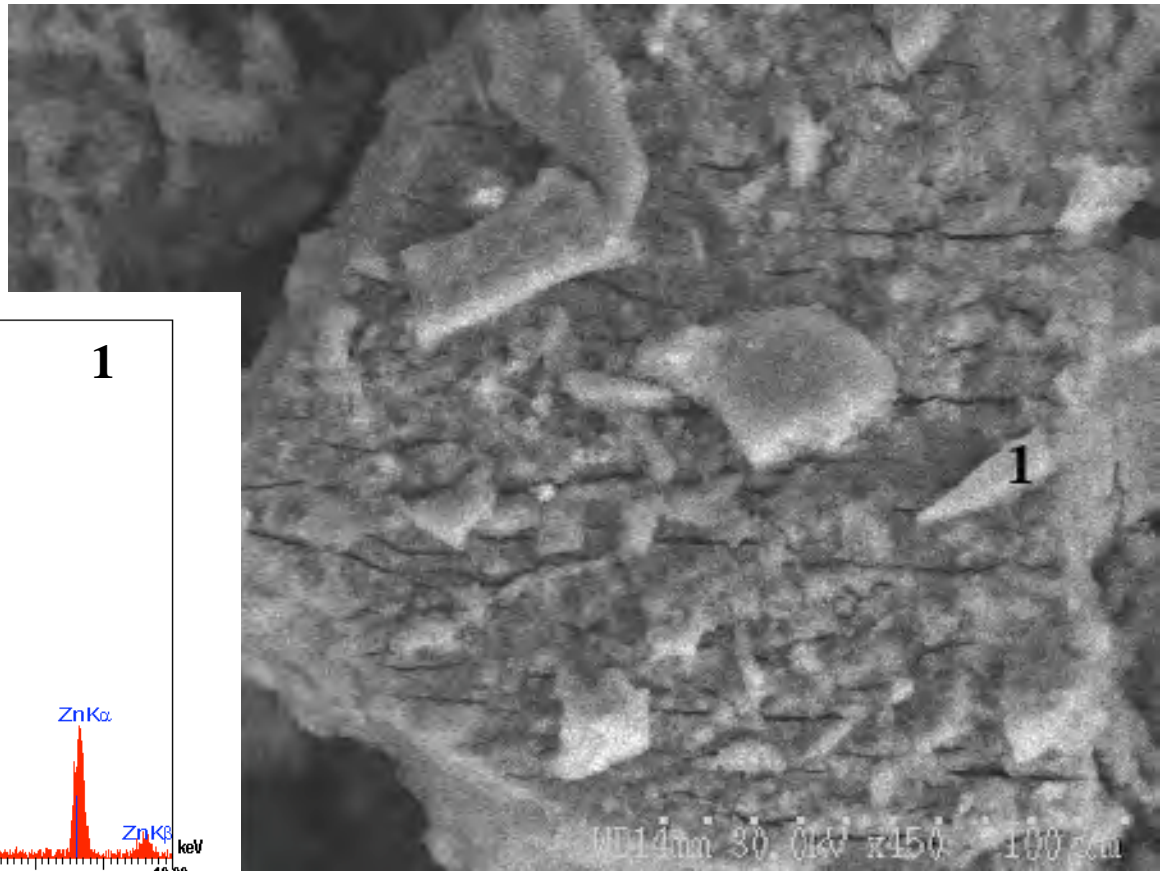
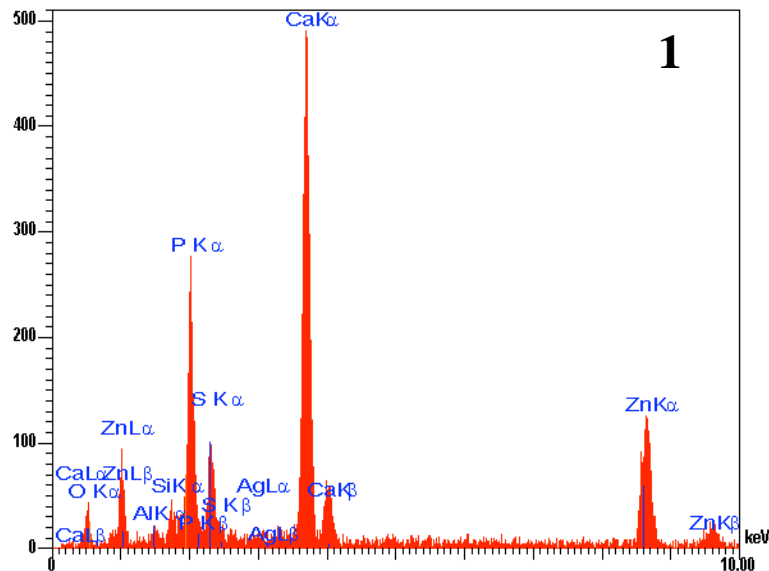
<u>Date</u>	<u>Entering Barrier (µg/L;ppb)</u>				<u>Exiting Barrier (µg/L;ppb)</u>			
	<u>pH</u>	<u>Cd</u>	<u>Pb</u>	<u>Zn</u>	<u>pH</u>	<u>Cd</u>	<u>Pb</u>	<u>Zn</u>
1/01	---	---	---	---	7.0	< 2	< 5	14
3/01	4.5	333	1,230	44,700	6.0	< 2	< 5	27
10/01	5.0	437	1,110	71,300	6.5	< 2	< 5	74
1/02	5.0	779	1,210	116,000	6.5	< 2	< 5	66
6/02	4.8	726	1,450	57,230	6.9	< 2	< 5	243
8/02	4.2	430	1,185	64,600	7.1	< 2	< 5	83
10/02	4.5	430	1,185	68,350	6.5	< 2	< 5	69
11/02	4.5	430	1,185	65,600	6.5	< 2	< 5	39
12/02	4.5	430	1,185	83,950	6.5	< 2	< 5	91
2/03	4.5	664	983	101,000	6.8	< 2	< 5	46
3/03	4.5	650	1,190	48,700	6.6	< 1	< 1	55
5/03	4.5	477	869	71,300	6.8	< 2	< 2	20
7/03	4.5	749	1,350	146,900	6.8	< 2	< 5	59
10/03	4.6	587	1,330	86,800	7.0	< 2	< 5	< 5
3/04	5.2	404	497	64,500	6.9	< 2	< 5	95
6/04	4.9	436	658	68,000	6.9	< 2	< 5	34

## Aqueous Chemistry of Groundwater Entering and Exiting the Apatite II PRB in August 2002

Species	Entering Barrier (mg/L;ppm)	Exiting Barrier (mg/L;ppm)	Species	Entering Barrier (mg/L;ppm)	Exiting Barrier (mg/L;ppm)
<i>pH</i>	<i>4.18</i>	<i>7.13</i>	Hg	<0.00005	0.0005
<i>Hardness</i>	78.8	125	K	1.27	1.54
<i>Alkalinity (CaCO<sub>3</sub>)</i>	<i>0</i>	<i>243</i>	Li	0.006	0.005
			Mg	3.27	3.39
<i>TDS</i>	344.9	466.9	<i>Mn</i>	<i>0.94</i>	<i>0.0022</i>
<i>Cond. (μS/cm)</i>	421	556	Mo	<0.001	<0.001
			<i>Na</i>	<i>3.54</i>	<i>5.06</i>
Ag	<0.0002	<0.0002	<i>NH<sub>4</sub></i>	<i>&lt;0.02</i>	<i>43.1</i>
<i>Al</i>	<i>3.16</i>	<i>0.020</i>	Ni	0.015	0.0021
As	0.0007	0.0004	NO <sub>2</sub>	<0.02	<0.02
B	0.008	0.012	<i>NO<sub>3</sub></i>	<i>0.58</i>	<i>&lt;0.02</i>
Ba	0.028	0.001	<i>Pb</i>	<i>1.16</i>	<i>0.0007</i>
Be	<0.001	<0.001	<i>PO<sub>4</sub></i>	<i>&lt;0.05</i>	<i>49.1</i>
Br	<0.02	<0.02	Rb	0.002	0.002
<i>Ca</i>	<i>26.0</i>	<i>44.5</i>	Sb	<0.001	<0.001
<i>Cd</i>	<i>0.42</i>	<i>&lt;0.001</i>	Se	<0.001	<0.001
<i>Cl</i>	<i>0.45</i>	<i>1.05</i>	Si	10.6	10.1
ClO <sub>3</sub>	<0.02	<0.02	SiO <sub>2</sub>	22.7	21.6
Co	0.0069	<0.001	Sn	<0.001	<0.001
CO <sub>3</sub>	<0.5	<0.5	<i>SO<sub>4</sub></i>	<i>216</i>	<i>&lt;0.05</i>
Cr	<0.001	<0.001	Sr	0.37	0.38
Cs	<0.001	0.001	Th	<0.001	<0.001
<i>Cu</i>	<i>0.23</i>	<i>0.0014</i>	Ti	0.006	0.036
<i>F</i>	<i>0.24</i>	<i>&lt;0.02</i>	Tl	<0.001	<0.001
Fe	0.05	0.11	V	<0.001	<0.001
<i>HCO<sub>3</sub></i>	<i>&lt;0.001</i>	<i>297</i>	<i>Zn</i>	<i>64.5</i>	<i>0.086</i>

**MINTEQA A2 modeling gives saturation indices that exceed 1 for:**

- sphalerite,  $\text{ZnS}$
- pyromorphite,  $\text{Pb}_5(\text{PO}_4)_3(\text{OH}, \text{Cl}, \text{F})$
- chlorapatite,  $\text{Ca}_5(\text{PO}_4)_3\text{Cl}$



**Photomicrograph of Apatite II from the first chamber showing biologically-mediated formation of micron-sized ZnS (sphalerite) crystals forming on surface of the Apatite II within the PRB.**



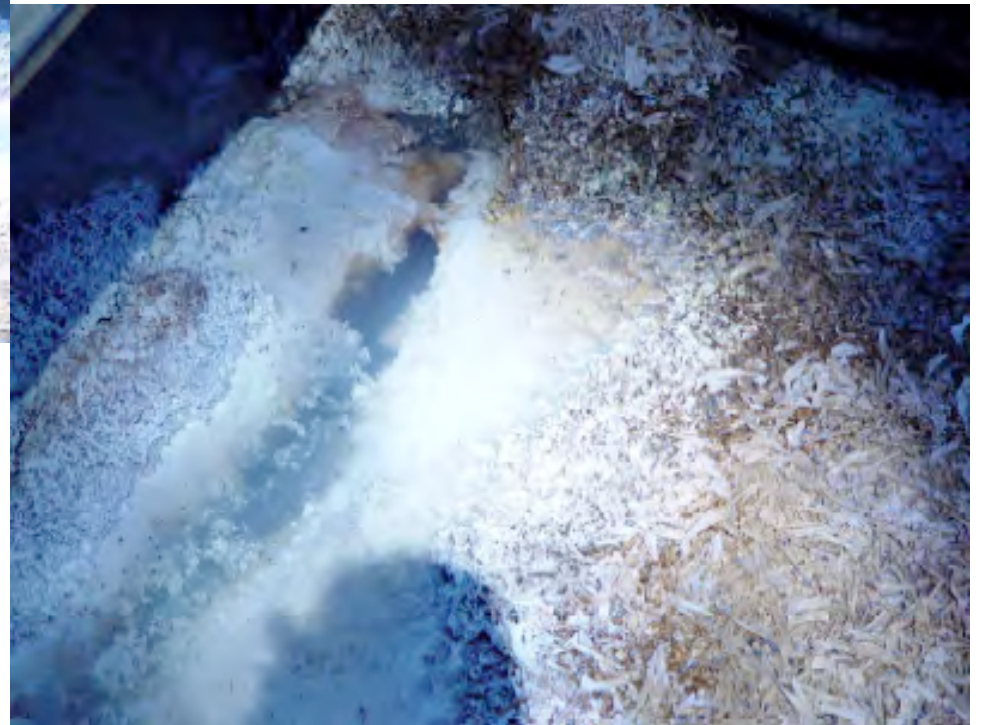
**Opening of the Success Mine PRB July 1, 2003**



*First Chamber of the West Cell*



**Note ZnS precipitation on surface and formation of voids and fast paths which have not yet compromise performance and are restricted to the first chamber.**



July 1, 2003

# Apatite II PRB Chambers

Inlet

1

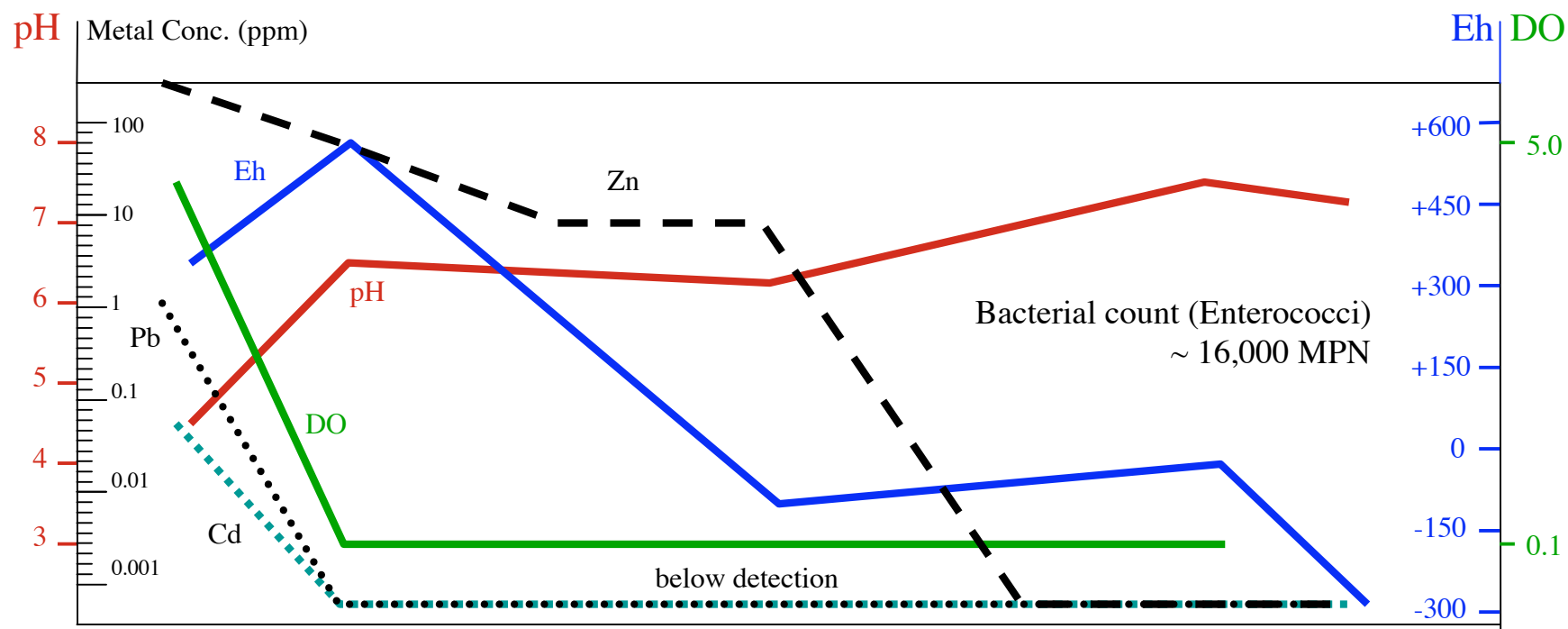
2

3

4

5

Outlet



Inlet [sulfate] = 216 ppm  
 [nitrate] = 0.58 ppm  
 [phosphorous] = 0.04 ppm  
 Bacterial count < 1 MPN

Outlet [sulfate] < 0.05 ppm  
 [nitrate] < 0.02 ppm  
 [phosphorous] ~ 9-10 ppm  
 Bacterial count < 1MPN



*Fifth Chamber of the East Cell*

**Based on periodic daily metal-loading averages from the Idaho State DEQ, the Apatite II PRB at Success Mine has sequestered**

- > 100 lbs of Cd,**
- > 150 lbs of Pb and**
- > 10,000 lbs of Zn**

**over the 3.5 years since it was emplaced.**

**Field investigations indicate less than 40% of the Apatite II is spent.**

# The Border Region



## Proposed Plan

**Chose a metal-contaminated site along the border that has several characteristics:**

- 1. water contaminated with Pb, Zn, Cd, NO<sub>3</sub>, SO<sub>4</sub> or any combination**
- 2. the water can be easily captured in a tank, trench or other type of PRB**
- 3. the effluent, now without metals, is able to be discharged to the ground, the subsurface, a river, or other type of drainage**
- 4. the influent and effluent can be monitored to determine performance**

## Proposed Plan

### Perform feasibility study at NMSU CEMRC:

1. with site water
2. consisting of column tests with Apatite II
3. to obtain performance data
  - reaction rates and residence times (optimal flow rates)
  - loading capacity (anticipated life-time)
  - effluent composition



## Proposed Plan

### Construct proto-type system (PIMS NW, Inc.):

1. size depends upon flow-rate (55-gallon or larger)
2. two-tanks: Apatite II + local sand
3. performance test
  - test range of flow rates
  - effluent composition
4. determine cost/unit

### Emplace at site

- Minimal training

Monitor for at least 6 months

Ascertain user interest/market

Determine other suitable sites

Transfer technology to local regions



## **Alternative Plan**

**Emplace as an pre-treatment step in a larger water-treatment system to remove metals, nitrate or sulfate, prior to any biological step**

- will lessen any need for metal treatment steps**
- will lessen need for pH buffering**
- will lessen nutrient additives**
- should greatly reduce operating costs and increase efficiencies**
- Amount of Apatite II depends upon throughput rate**

# Case History

## Camp Stanley Storage Activity (CSSA)



- ◆ Boerne, Texas, north of San Antonio
- ◆ Base is a former site for open burn/open detonation activities and earlier military activities beginning in 1906
- ◆ Soils excavated and sifted for removal of UXO were found to be contaminated with lead.

# Aerial view of Camp Stanley



**Sieving to Remove UXO Resulting in Piles of  $< 3/8$ -inch  
Pb-contaminated Soil at Various Sites around CSSA**

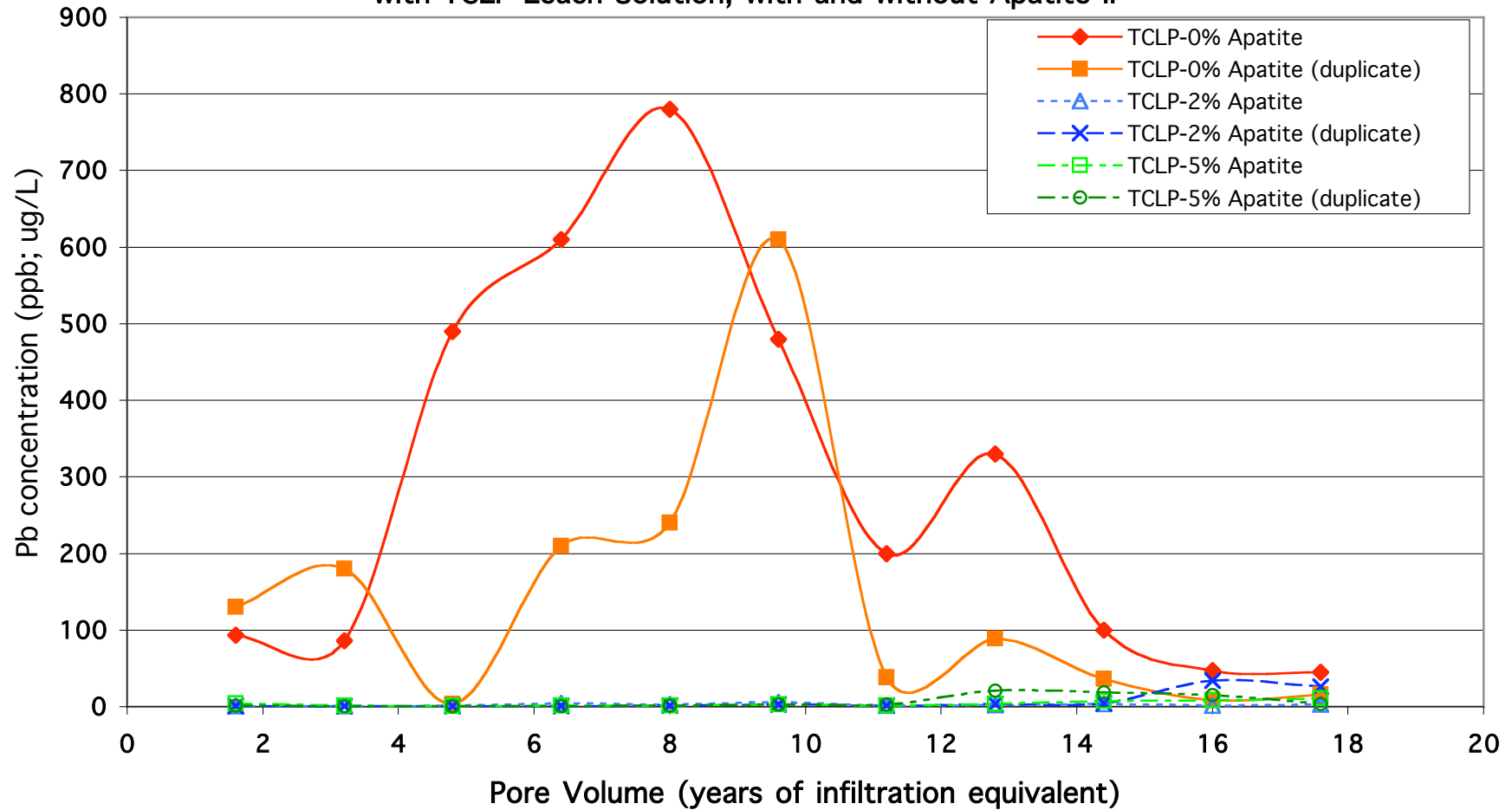


# Field Implementation

- ◆ Feasibility Study (FY2000)
- ◆ Field Implementation (FY2001)
  - Site Preparation
  - Apatite II Soil Mixing (3%)
  - 6'' Clean Soil Cover Placement
  - Plant Natural Vegetation
- ◆ Monitoring (FY2002-2004)
  - Leachate Collection From Shallow Lysimeters
  - Bioavailability (in-vitro)
- ◆ Regulatory Acceptance (FY2005-2006)
  - Bioavailability (*in vitro* and *in-vivo*)

# Feasibility Study

Camp Stanley B20 Pb-Contaminated Soils Column Tests  
with TCLP Leach Solution, with and without Apatite II



## Site Preparation - removal of surface vegetation



## Mixing Apatite II into soil (3% by weight)



## Spreading treated soil over one-acre site



## Spreading clean soil cover over site



## Final site prior to seeding



# Emplacing Shallow Monitoring Wells



## Wildflowers in bloom - remediation complete



# Field Characterization Results - TCLP batch tests

## Camp Stanley SWMU B20 PIMS Field Study Results

	Total Pb (mg/kg)	Untreated TCLP Pb (mg/L)	Apatite II-treated TCLP Pb (mg/L)
Range	200 to > 8,000	1.07 to 3.22	0.17 to 1.23
Average	1,942	2.1	0.485

## Waste Classification Criteria for Pb based upon TCLP

RCRA Hazardous Level is  $\geq 5$  mg/L Pb

State of Texas Class 1 Non-Hazardous Level is 1.5 to 5 mg/L Pb

State of Texas Class 2 Non-Hazardous Level is  $\leq 1.5$  mg/L Pb

## Field Leachate Monitoring of Pb

- ◆ Leachates from Apatite II-treated & untreated soils
- ◆ Collected from shallow lysimeter wells
- ◆ Determine potential impact to groundwater

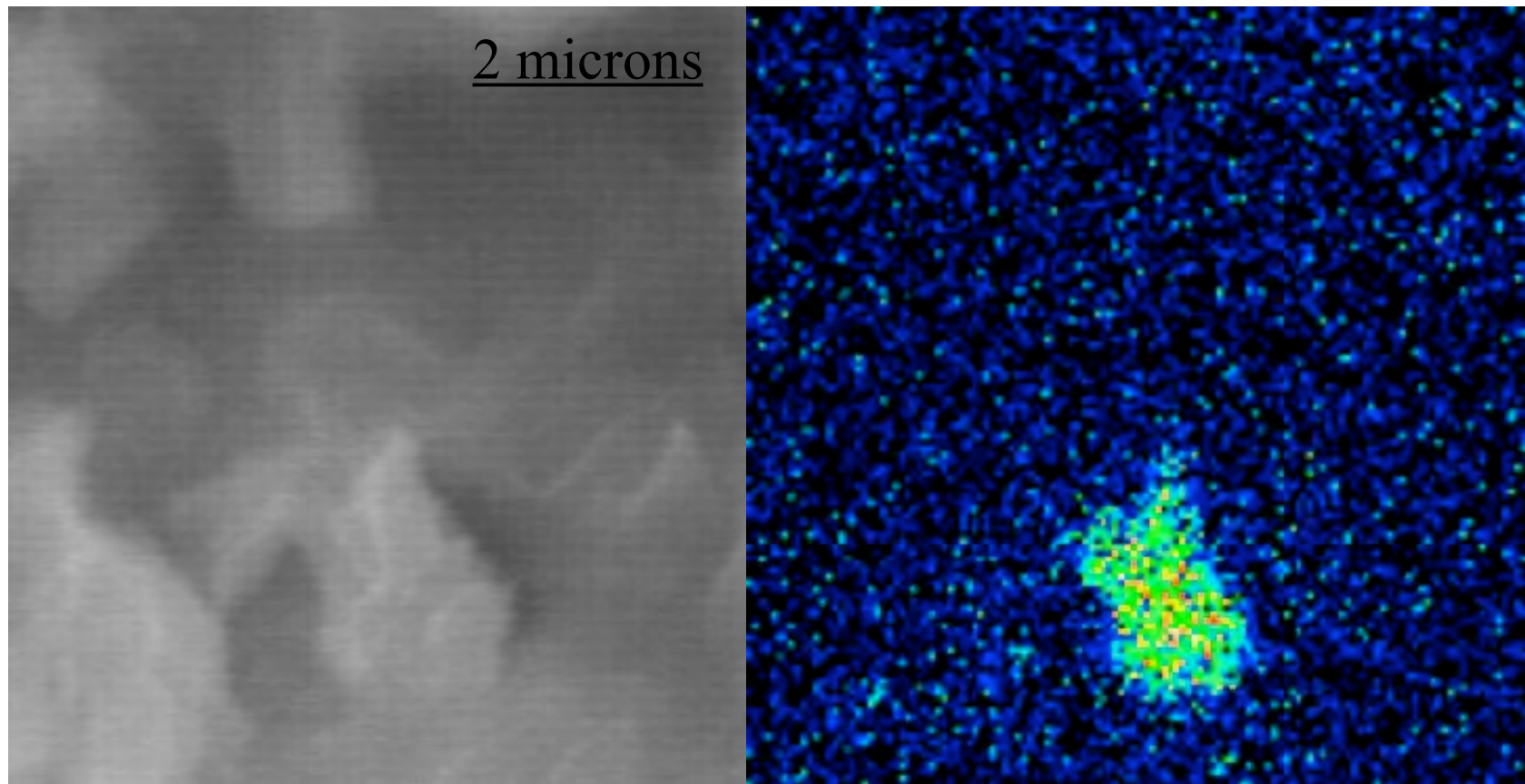
Two-year average of  
Apatite II-Treated soil  
mg/L Pb

***0.007***

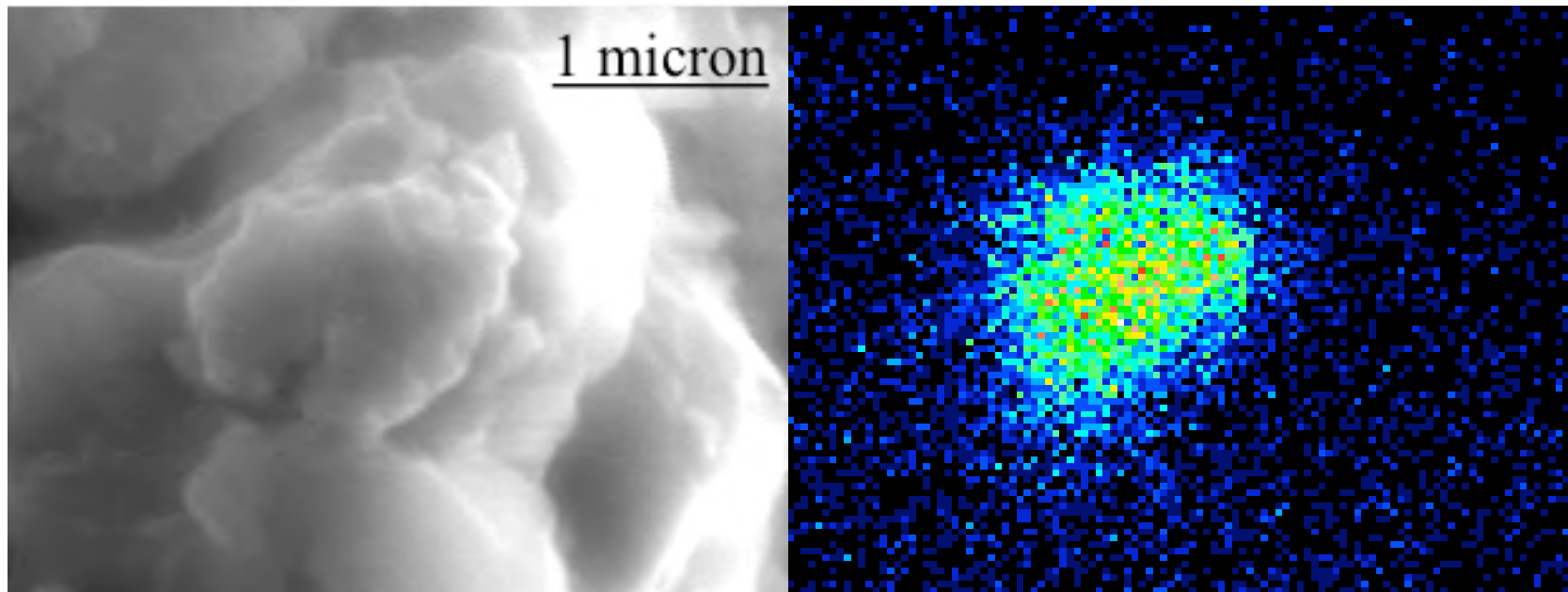
One-year average of  
Untreated soil  
mg/L Pb

***0.280***

*MCL for Pb = 0.015 mg/L*

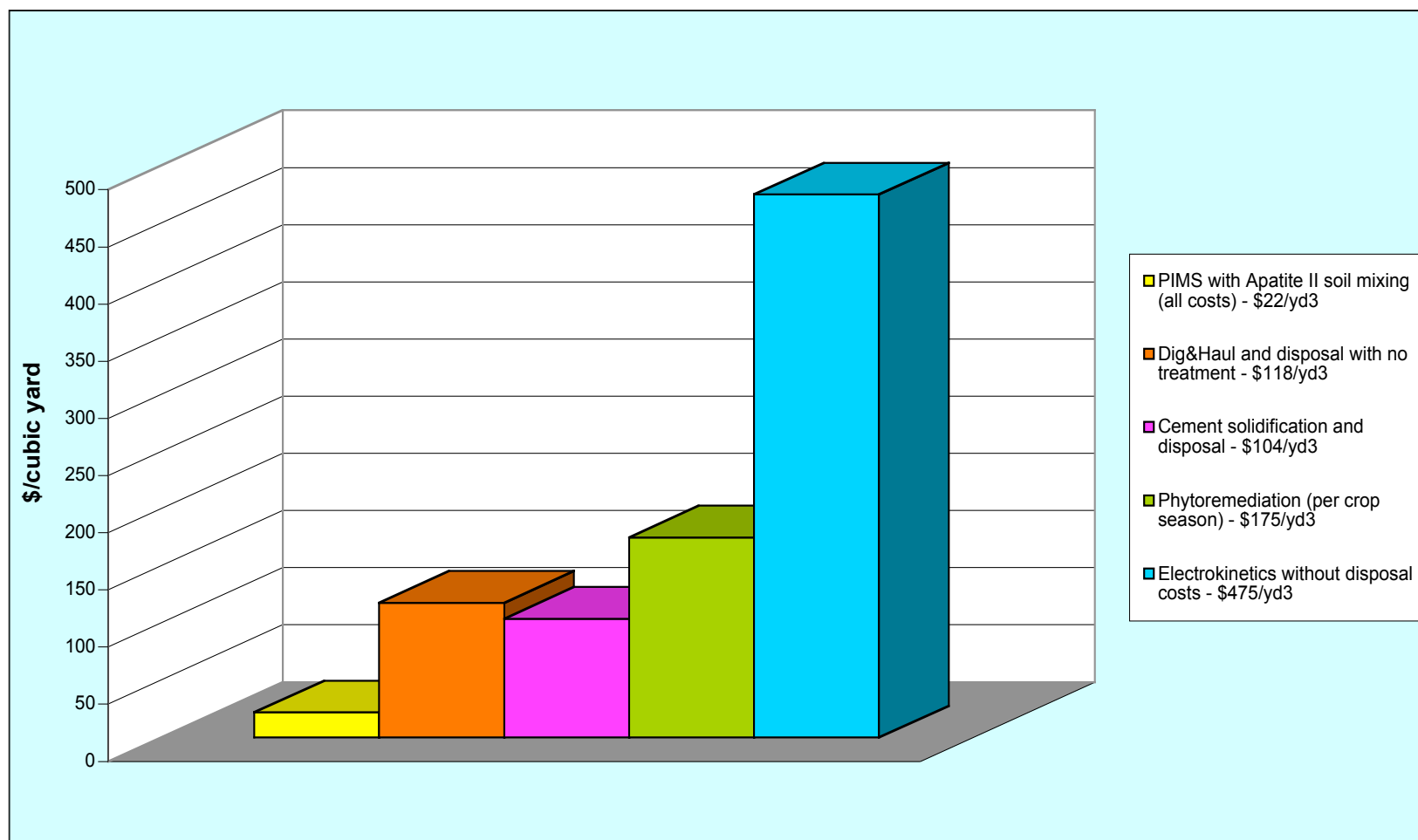


**Left: Photomicrograph of PIMS-treated Camp Stanley range soil with a micron-sized Pb grain attached to the surface of the Apatite II. Right: Pb X-ray map.**



**Left: Photomicrograph of PIMS-treated Camp Stanley range soil with a micron-sized Pb grain attached to the surface of the Apatite II.**  
**Right: Pb X-ray map.**

# Cost effectiveness of remedial technologies for Pb at Camp Stanley SWMUs\*



\*Parsons, Inc.

## Field Results

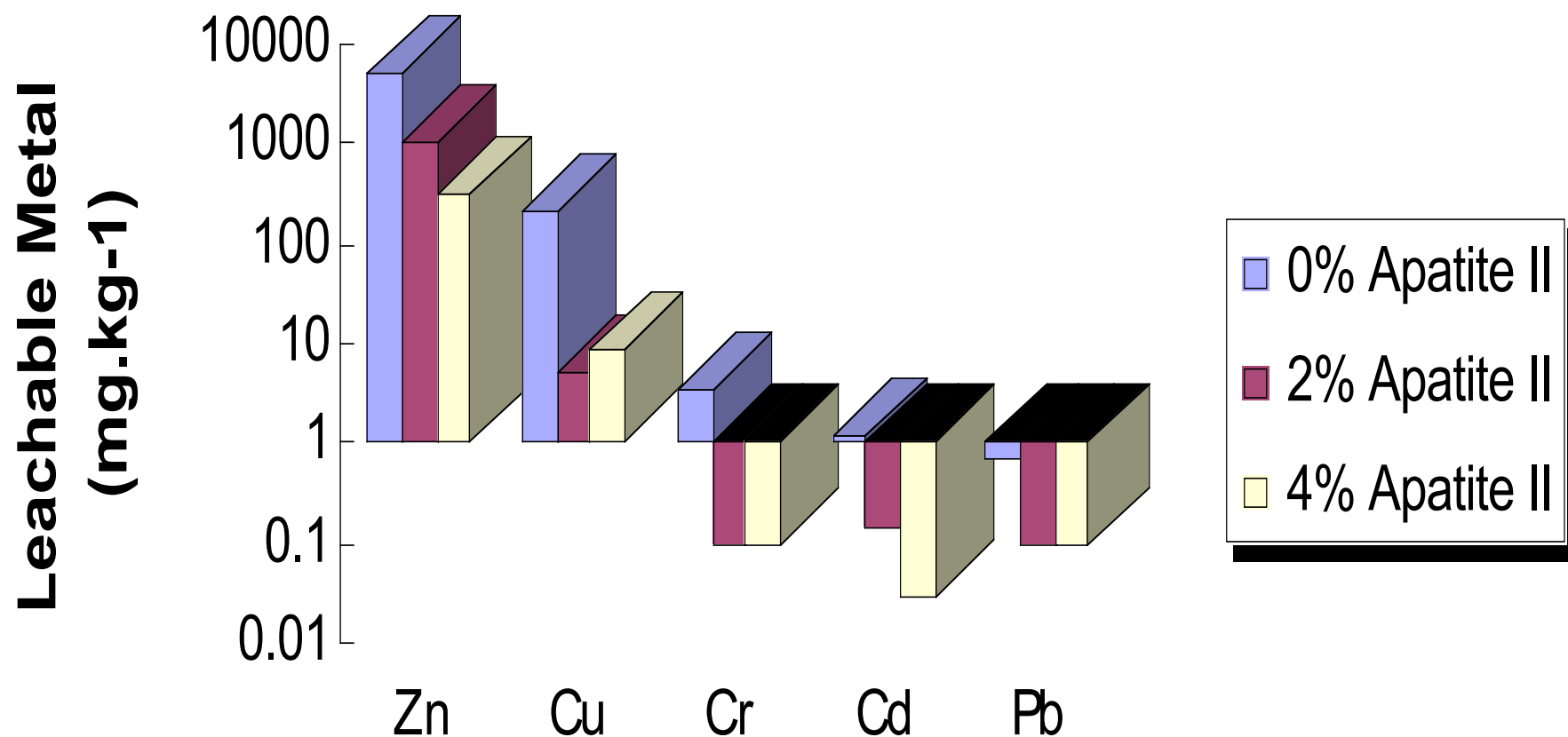
- ◆ **No soluble lead leaches from treated soil**
- ◆ **Reduced classification of contaminated soil to State of Texas Class 2 non-hazardous levels**
- ◆ **Reduced bioavailability of Pb in treated soil**
- ◆ **Total costs for treatment were \$22/yd<sup>3</sup>**

# **Case History: British Fertilizer Plant**

- **Highly acidic soil (pH 2.5)**
- **Multiple metal contamination:**  
**Zn 4670, Pb 1800, Cu 260, Cr 20, Cd 8 mg.kg<sup>-1</sup>**
- **Pilot scale test:**  
**soil mixed with 0%, 2% or 4% Apatite II**
- **Monitor leachable metal**

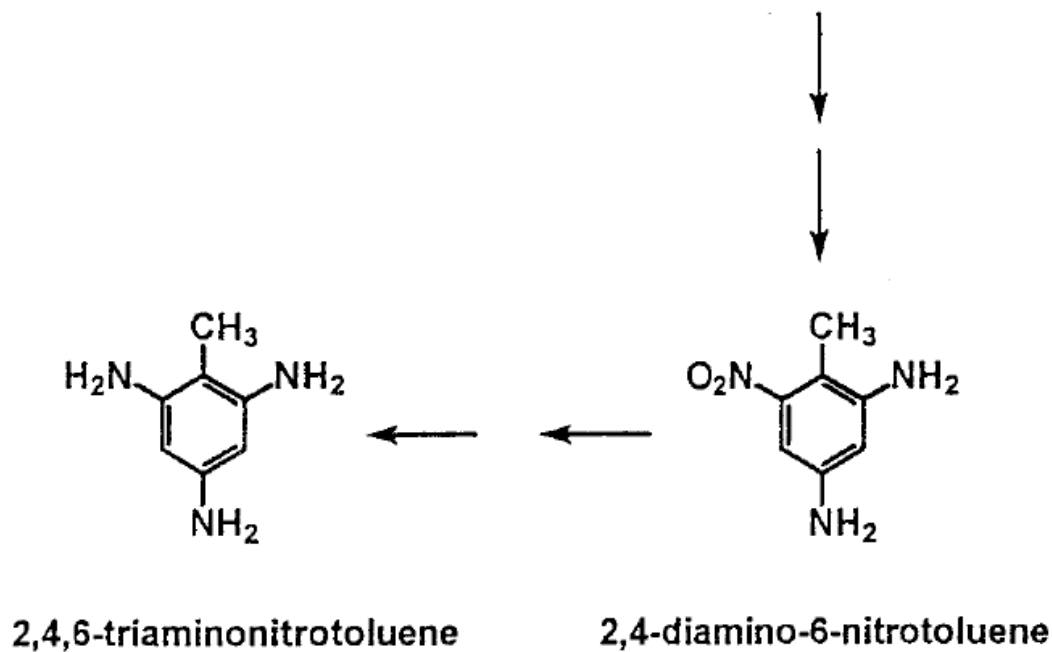
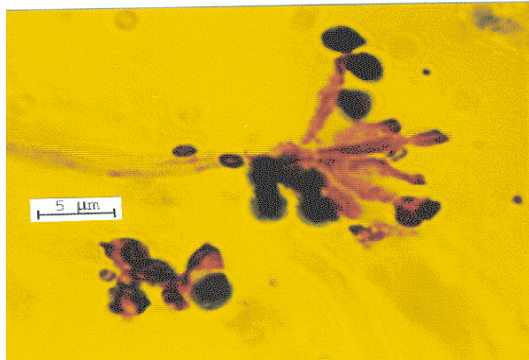
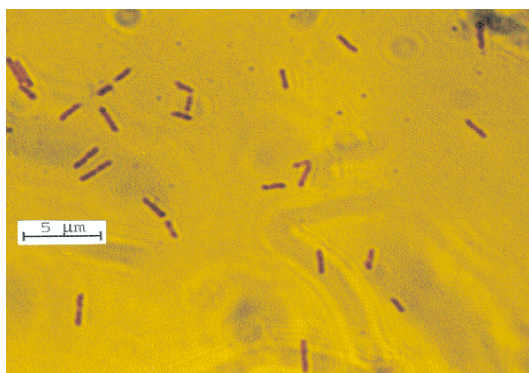


## Fertilizer Plant - pilot data (week 8)



**Apatite II readily stimulates the microbial degradation of compounds such as TNT and RDX, particularly with specific gram-negative bacteria and fungi.**

## Transformation of TNT via sequential reduction



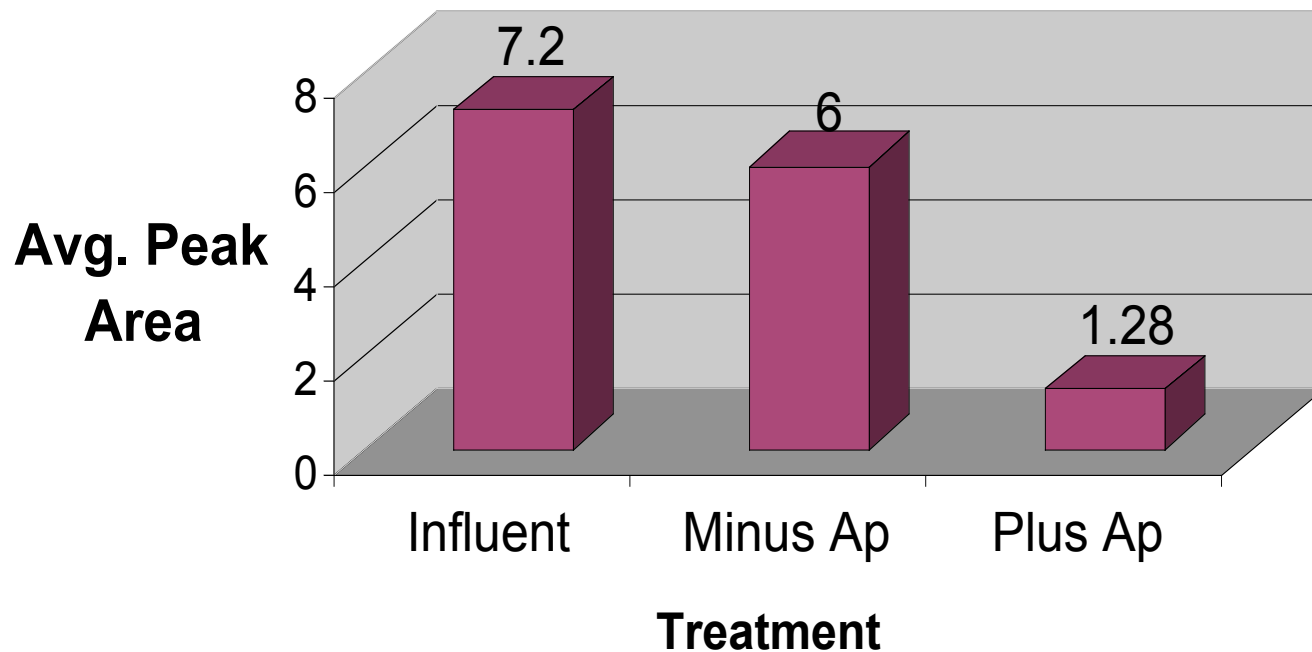


# APATITE II REACTIVE BARRIER PILOT TEST FOR HE REMOVAL

SAMPLE #	DESCRIPTION	RDX ppm	TNT ppm	HMX ppm
104702-0	TNT-H2O influent ~0.5ppm	0.38	0.39	0.034
104702-1	Effluent Sample	<0.01	<0.01	0.02
104702-2	Effluent Sample	<0.01	<0.01	0.02
104702-3	Effluent Sample	<0.01	<0.01	0.10
104702-4	Effluent Sample	<0.01	<0.01	0.01
104702-5	Effluent Sample	<0.01	<0.01	0.09
104702-6	Effluent Sample	<0.01	<0.01	0.16
104702-7	Effluent Sample	<0.01	<0.01	0.15
104702-8	Effluent Sample	<0.01	<0.01	0.04
104702-9	Effluent Sample	<0.01	<0.01	0.06
104702-10	Effluent Sample	<0.01	<0.01	0.07
104702-11	Effluent Sample	<0.01	<0.01	0.06
104702-12a	Effluent Sample	<0.01	<0.01	0.02
104702-12b	Effluent Sample	<0.01	<0.01	0.05
104702-13a	Effluent Sample	<0.01	<0.01	0.10
104702-13b	Effluent Sample	<0.01	<0.01	0.08
104702-14a	Effluent Sample	<0.01	<0.01	0.08
104702-14b	Effluent Sample	<0.01	<0.01	0.03
104702-15	Effluent Sample	<0.01	<0.01	0.03
104702-16	Effluent Sample	<0.01	<0.01	0.02
104702-17	TNT-H2O influent ~0.5ppm	0.39	0.28	0.031

2-week run residence time = 10 hours sample 0 and 17 = influent groundwater spiked with TNT, HMX and RDX  
 10% MeOH by volume added to each sample container to prevent precipitation or sorption on container walls

**Table 1: Average Samples of TNT in  
Columns 5,6,7, and 8**



**Average samples of soil columns with  
and without Apatite II (Ap) infused with  
TNT-contaminated groundwater.**